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<b>14. ABSTRACT</b>  <p>This report results from a contract tasking Francevych Institute for Problems of Materials Science as follows: The Project will derive new scientific knowledge on in-situ titanium composite materials. This understanding is required to develop new improved composites achieving enhanced heat resistance, specific strength and stiffness as well as plasticity up to 3% elongation. This new knowledge will be obtained by studying in detail features of formation of structure in dependence on chemical composition and methods of alloy producing and processing as well as the relationship between microstructures and mechanical properties.</p> <p>Titanium in-situ composites with alpha-matrix, with alpha + beta- and beta-matrix as well as with intermetallic (Ti<sub>2</sub>AlNb, Ti<sub>3</sub>Al etc) matrix based on Ti-Si-X and Ti-B-X systems strengthened with complex boride, silicide and intermetallic phases are chosen. Structure and mechanical behavior of as-cast, plastically deformed and heat-treated alloys and their dependence on alloying, modifying, overheating and solidification rate will be subjected to characterization with electron microscopy and related techniques, and mechanical tests under bend and uniaxial tension in a wide temperature range embracing their brittle, brittle-to-ductile transition and ductile states.</p>					
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**The Project P-060****THE STUDY OF STRUCTURE FORMATION AND MECHANICAL  
BEHAVIOR OF HEAT-RESISTANT TITANIUM ALLOYS WITH  
EUTECTIC STRENGTHENING****(2000-2004)****The Final Report****CONTENT**

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## 1. INTRODUCTION

The basic research oriented on creation of scientific basement of developing materials of high specific strength and stiffness is related yet to the significant priorities acknowledged worldwide. As the objects for study are materials of low specific weight where alloys based on titanium are paid particular attention. The relatively high melting temperature (1660 °C) and oxidizing resistivity (~600 °C) allow to be achieved potentially. The alloys based on nickel in spite of their lower melting temperature (1455 °C) may be used at temperatures 900 – 1000 °C. Comparatively low heat resistance of titanium alloys results from relatively low Young modulus (~112 GPa) and polymorphous transformation at 882 °C, where modulus of elasticity and strength decrease remarkably. Conventional titanium alloys are not able to work at temperatures above 600 °C.

The preliminary researches by authors of the Project done with some alloys of the Ti-Si-X-system have shown that due to eutectic crystallization the silicide frame is formed. This silicide frame may be considered as natural composite and, accordingly, heat resistance of such the systems may be increased significantly. Another attractive candidate to search optimal compositions, according to the Crossman's data, is the Ti-B-system.

Titanium in-situ composites with  $\alpha$ -matrix, with  $\alpha+\beta$ - and  $\beta$ -matrix as well as with intermetallic ( $\text{Ti}_2\text{AlNb}$ ,  $\text{Ti}_3\text{Al}$  etc) matrix based on Ti-Si-X and Ti-B-X systems strengthened with complex boride, silicide, and intermetallic phases were chosen. Structure and mechanical behavior of as-cast, plastically deformed and heat treated alloys in dependence on alloying, modifying, overheating and solidification rate were be subjected to characterization with electron microscopy and related techniques, and mechanical tests under uniaxial tension and bend in wide temperature range embracing their brittle, brittle-to-ductile transition and ductile states.

As the result of this comprehensive study giving the rich picture of structure and mechanical behavior was done and the structural concept of titanium in situ composites to achieve the best balance between their strength and ductility was developed.

The Project was fulfilled for three years. The first year efforts were directed on the study of Ti in-situ composites with  $\alpha$ -matrix. The second and the third years must be devoted to studying Ti composites with  $\alpha+\beta$ -,  $\beta$ - and intermetallic ( $\text{Ti}_2\text{AlNb}$ ,  $\text{Ti}_3\text{Al}$  etc) matrixes.

Initially, the Project P-060 was pursuing deriving new scientific knowledge on in situ titanium composites and understanding, which is required to develop new improved composites achieving their enhanced heat resistance, specific strength and stiffness as well as room temperature plasticity up to 3% elongation via studying in detail features of formation of structure in dependence on chemical composition and methods of alloy producing and processing as well as relationship between microstructures and mechanical properties.

Frantcevykh Institute for Problems of Materials Science (FIPMS) of National Academy of Science of Ukraine and National Metallurgical Academy (NMA) of Ukraine were as Participating Institutions in partnerships with Materials and Manufacturing Directorate of Air Force Research Laboratory.

## 2. THE OBJECTIVES OF THE PROJECT

The objectives of the Project were as follows:

- To study of the phase equilibrium in the Ti-Si-X and Ti-B-X systems alloyed with different alloying and modifying elements. The search will be directed on an increase of both heat resistance and plasticity. The detailed study of "titanium corners" of diagrams will be done.
- To investigate an influence of alloying and modifying elements on morphology and size of strengthening phases.
- To find dependencies of structural parameters on solidification conditions.
- To investigate an effect of heat treatment on structure and properties of selected alloys.
- To study structure and properties (hardness, yield stress, strength under bending and tension, fracture toughness in a wide temperature range) of selected groups of alloys.
- To study features of transition of these groups of materials from a brittle state into a ductile one, particularly fracture mechanisms change, initiation of cleavage, relation between plasticity and cleavage, pores nucleation, temperature limits of a brittle-to-ductile transition.
- To investigate an effect of plastic deformation on structure and mechanical behaviour of selected alloys in a wide temperature range.

After discussion of data obtained for the first year of work the Project Manager focused the Objectives on the room temperature plasticity (4 % of elongation) in a complex with high strength and high stiffness on account of some worsening of high temperature properties. The Tasks of the second and third years were reformulated to achieve the goals as follows:

To elaborate thermo-mechanical processing of big ingots selected in accordance with data obtained for previous research, which could meet:

- Room temperature plasticity – higher 4 % of elongation;
- Strength at temperature 600 °C – higher 500 MPa at tension;
- Room temperature elasticity modulus – higher 140 GPa;
- Room temperature fracture toughness  $K_{Ic}$  – higher 30 MPa·√m.

## 3. MATERIALS AND METHODS

All the Ti-based in situ composites studied are divided roughly for three big groups namely:

- 1) To build phase equilibrium diagrams. Ingots were smelted on a base of iodine titanium with arc and were small, of a few grams of weight. Additives were changed in a wide range of amounts as usual.
- 2) To estimate influence of selected alloying and modifying chemical elements (Al, Zr, Nb, Mo, rare earth elements etc. chosen with literature available and own experience) on mechanical properties of as-cast state small cylindrical ingots, size of which is enough to make only one sample for tensile test, were smelted with arc method in vacuum ( $10^{-3}$  torr, oil diffusion pump) using iodine titanium as a base. Size of ingots was around 15 mm diameter and 80 mm length, ~80 g weight.

To estimate influence of thermo-mechanical treatment on structure and mechanical behavior of composition selected being based on the data obtained as above-mentioned large ingots of 60 mm diameter and 150-600 mm size were smelted on a base of commercial pseudo- $\alpha$  alloy BT1-0 (Fe<0.25; Si<0.1; C<0.07; N<0.04; O<0.2; others<0.3 wt. %) with plasma-arc equipment in argon atmosphere. The BT1-0 alloy has coefficient of  $\beta$ -phase stabilization  $k_\beta = 0.05$  [1, 2].

- 3) Big ingots of complex alloyed alloys were tested too. Temperature of the smelt of these alloys was between 1620-1660 °C. Liquid metal was decanted into graphite mold inside of melting chamber. Obtained ingots were cooled to 600 °C inside of chamber and after that to room temperature in air outside of equipment.

Alloys were forged in such a way. Their blanks were turned to cylinders of 58 mm diameter, sealed in steel pipe, and heated at first from room temperature to 900 °C in electric air furnace together with it during 1 hour. After that blanks were carried manually from the electric furnace into gas one where they were heated up to 1100 °C. Blanks heated at this temperature for 1 hour were forged manually to 90 % power of deformation. Another deformation routes including rolling were used too, they are analyzed below.

In some cases rolling and profile rolling with similar time and temperature regime were applied too

Cylindrical specimens with fillets were used for mechanical tests at uniaxial tension. Their working length and diameter were 15 mm and  $3 \pm 0.01$  mm respectively. Surface of their working part was polished with diamond abrasive.

Uniaxial strength and elongation at the loading rate of  $1.2 \cdot 10^{-3} \text{ s}^{-1}$  in the temperature range of 20–800 °C were measured in air with universal testing machine U2 manufactured by NIIKIMP, the Russian Federation.

Bending four points' tests including for Young modulus measurements were done with the CeramTest machine produced by Institute for Problems of Strength, Kyiv, Ukraine. Rectangular samples of 3.5 x 5.0 x 50 mm. Distance between rolls are 20 and 40 mm. The displacement sensor was attached to samples. Loading rate was 0.2 mm/min. Accuracy of measurement of mechanical properties was better 1 %.

Fracture toughness  $K_{Ic}$  was measured in accordance with the GOST 25.506-85 standard with samples of 2.5 x 5.0 x 35 mm at three points' bending static test. As initiating crack the brittle cracks nucleated at electro-spark cutting of notching was used. Tip of notch has length ~2.5 mm and radius ~0.08 mm.

Hot hardness was measured with the hardness tester UHT-2 equipped with Vickers sapphire indenter produced by IPMS, Ukraine. Hardness was measured at 1 kg load for 1 hour at 600, 700 and 800 °C. Samples were annealed at 800 °C for 2 hour before testing.

Microstructure and distribution of chemical elements along it as well as fracture mechanisms were studied with scanning electron microscopy (SEM) and X-ray microanalysis (XRMA) using Superprobe-733, JEOL, Japan. X-ray diffraction phase analysis was done with DRON-3M diffractometer, "Burevestnik", Russian Federation, and HZG-4a, Germany, in monochromatic  $\text{CuK}\alpha$  radiation with polished samples of min 12 mm diameter.

Structure was revealed with so-called deep electrolytic etching with an etchant based on acetic acid of polished samples. This approach is giving an idea of strengthening particles morphology with SEM and improving detectability of chemical elements with XRMA at their qualitative analysis. Some selected samples were studied with transmission electron microscopy of thin films (TEM) and selected area electron diffraction pattern (SADP) and XRMA of thin films with TEMSCAN 100CXII, JEOL.

#### 4. DATA OBTAINED AND THEIR DISCUSSION

Research in field of phase equilibrium in the Project was based on known binary Ti-Si and Ti-B diagrams, which have taken into account also some important studies in this field of other authors [1-10].

Alloying with Al, Zr, Sn, Nb, V, and Ge was chosen for the study. The choice of these elements was determined by the reasons as the next:

Alloying with Al and Zr is allowing increasing significantly strength and heat resistance of alloys with  $\alpha$ -matrix; alloying with V and Nb was directed on the study of with  $\alpha$ -,  $\alpha+\beta$ - and  $\beta$ -matrixes; Sn is used in many Ti alloys as an alloying element, besides that it forms rather high temperature eutectics; Ge was chosen as an analog of Si. Besides that the study of Ti-Ge-B and Ti-Si-B diagrams was done. The special attention was given to the titanium corner because the Project was oriented in general on development of in situ composites with titanium matrix reinforced with silicide and boride phases.

As it is known the eutectic solidification takes place in the field of our interest where Ti-Ti<sub>3</sub>Si<sub>3</sub> and Ti-TiB form in the solid state. Ti-B-system is depicted as more simple because there is low solubility of boron in solid state in comparison with Ti-Si-system where some solubility of silicon takes place both in  $\beta$ - and  $\alpha$ -matrixes. E.g., maximal solubility of silicon in  $\beta$ -phase at 1350 °C is 4.5-at. % and 0.8-at. % in  $\alpha$ -phase at temperature of eutectoid transformation. The eutectoid transformation in binary system takes place at 865 °C.

It is possible to note a significant analogy with the Ti-C-system. The difference consists in the next: carbon in iron is an interstitial impurity; however silicon in titanium is a substitutional one. In the rest, the analogy is so deep that it is possible to speak about development of both "titanium cast irons" and "titanium steels" (in Ti-Si-X-system) (see below and in reports on the first and the second years of work, tasks 1 and 9). Suited chapters of the report give rather full data on phase equilibrium of multicomponent systems studied. Short description of data obtained for titanium corners of systems studied is given below. They were taken into account in study of structure and properties of selected multicomponent alloys in as-cast and deformed states.

##### 4.1. Ti-Si -SYSTEM

###### 4.1.1. Phase equilibrium diagrams

The Ti-Si is a prospective basic system for elaboration of high-temperature alloys with combination of strengthening mechanisms. The mechanical properties of these materials to great extent depend on the topology of appropriate phase diagrams (solubility of the components in the phases of interest, configuration of the boundaries of homogeneity ranges of the individual phases, location of the monovariant curves and invariant points, the character and the temperatures of phase transformations) in the concentration intervals of interest. Systematic information on the multicomponent phase diagrams is absent. Thus, the goal of this work was to obtain reliable comprehensive self-consistent results on the phase relationships in the systems, which could be prospective for elaboration of the materials on the basis of Ti-Si eutectic. Its structure is shown in Fig. 1.

Examination of the phase composition of hypoeutectic binary, ternary and quaternary samples annealed according to the scheme 1300°C/30 h + 1000°C/30 h + 800°C/30 h has confirmed thermodynamic stability of the Ti<sub>3</sub>Si compound. However, kinetics of formation of the Ti<sub>3</sub>Si phase is such that it does not present in the ternary and multicomponent samples even after annealing of as-cast samples at 800 °C/100 h. So, for the practical usage one can use metastable



diagrams, where this phase and transformations with its participation can be ignored. Exceptions are Ti-Nb-Si-based alloys.

Isothermal sections at 1200 – 800 °C and isopleth at 10-at. % Si of the Ti-corner of the Ti-Si-Al system were constructed. The  $Ti_3Si$  phase was shown to participate in equilibrium up to ~16-at. % Al. However, for the practical usage, as shown above, it can be ignored. Then up to ~10-at. % Si the two-phase field  $\alpha + Ti_5Si_3$  exists, where no phase transformations occur below ~1000 °C. Thus, this field is appropriate as a basis for high temperature materials.

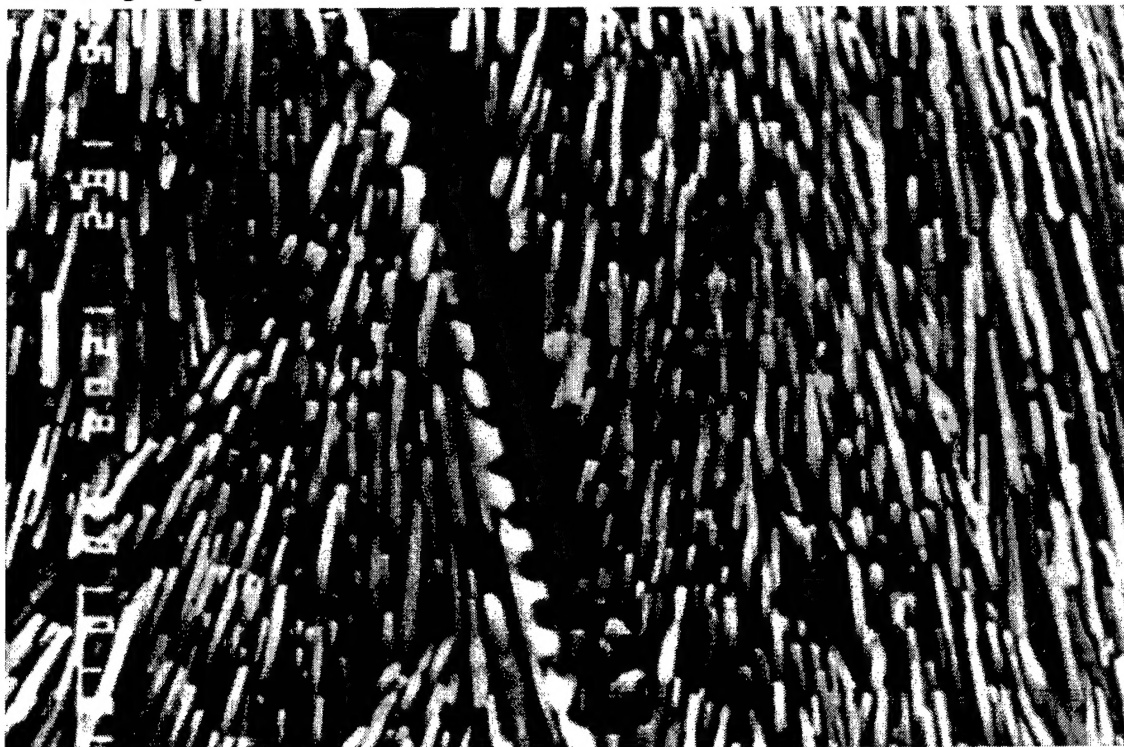


Figure 1. SEM appearance of Ti-8.5Si eutectic alloy after deep etching.

The **Ti-Si-Sn** system was studied at crystallization and in the solid state. Three more important features of the system are as follows:

- Existence of the ternary compound T ( $Ti_5Si_{1.2-1.6}Sn_{1.8-1.4}$ ), which was found for the first time. The structure was resolved in the structure type  $W_5Si_3$ .
- Existence of the ternary eutectic  $L \leftrightarrow \beta + \langle Ti_3Al \rangle (\alpha_2) + \langle Ti_5Si_3 \rangle$ .

Similar to the ternary Ti-Si-Al system, in the quaternary **Ti-Si-Sn-Al** one ignoring the phase fields with participation of the  $Ti_3Si$  phase results in appearance of wide  $\alpha + Ti_5Si_3$  region below 800-900 °C, where no phase transformations occur. This field is appropriate for elaboration of the alloys with different ratio of  $\alpha$  and  $Ti_5Si_3$  phases. However, tin decreases a little the  $\alpha \leftrightarrow \beta$  transformation temperature of Ti. So, in respect of high-temperature properties high additions of tin to the Ti-Si-Al alloys are not desirable. Its content should meet the demands of workability.

In the **Ti-Zr-Si** system existence of the ternary compound  $(Ti,Zr)_2Si$  ( $Ti_2Si$ ) was confirmed. This was shown to form by peritectic reaction. The three-phase field  $\beta + Ti_5Si_3 + Ti_2Si$  forms by invariant eutectic equilibrium. The coordinates of the invariant point E were determined to be

1330 °C and ~78Ti-11Zr-11Si. In the solid state the three-phase field  $\alpha+\beta+\text{Ti}_2\text{Si}$  exists with the temperature decreasing when Zr concentration increases. Thus, at Si concentrations outside its solubility in the  $\langle\text{Ti,Zr}\rangle$  solid solution, increasing of Zr concentration should decrease the high-temperature properties of the alloys.

The long-term hot hardness measurements for the alloys Ti-Zr-10Si have shown, that below 550 °C this depends on dispersity of the structure, while above this temperature this depends on the temperature of  $\alpha\leftrightarrow\beta$  transformation.

Examination of the **Ti-Zr-Si-Al** system has shown that at stable Al or Zr concentrations equal to 5 at. %, the system behaves similar to the ternary Ti-Zr-Si or Ti-Si-Al, respectively. The isopleth at 5 at. % Si + 5 at. % Al is similar to those of the ternary Ti-Zr-Si system, while the temperatures of the  $\alpha+\beta+\text{Ti}_2\text{Si}$  three-phase field in the quaternary system is about 100 °C higher than in the ternary one.

Aluminum addition to the ternary Ti-Zr-Si alloys results in significant strengthening of both Ti-matrix and  $\beta+\text{Ti}_2\text{Si}$  eutectic when Zr concentration increases. In the case of eutectic this is in contrast with ternary Al-free alloys.

In contrast to the above systems, in the **Ti-Nb-Si-Al** system the  $\text{Ti}_3\text{Si}$  silicide can be an equilibrium phase up to the liquidus temperatures, depending on Nb concentration. These results from the fact that  $\text{Ti}_3\text{Si}$  and  $\text{Nb}_3\text{Si}$  form continuous solid solution, while  $\text{Nb}_3\text{Si}$  forms from the liquid and exists in a narrow temperature interval, and  $\text{Ti}_3\text{Si}$  forms in a solid state. Thus, in the alloys Ti-(2.5-17.5)Nb-(4-10)Si-5Al, step-by-step annealed from sub-solidus temperature down to 800 °C peritectoid reaction  $\beta+\text{Ti}_3\text{Si}_3 \leftrightarrow (\text{Ti,Nb})_3\text{Si}$  was unfinished. In the alloys (81.5-61.5)Ti-3.5Nb-5Si-(10-30)Al, annealed at 800°C/100 h just after casting, the  $\text{Ti}_3\text{Si}$  phase was not observed, and in the alloys (83.5-81.5)Ti-(5-8)Nb-6.5Si-5Al it was present after all thermal treatments.

Increasing of Nb concentration resulted in stabilization of the  $\beta+\text{Ti}_3\text{Si}$  region down to at least 800 °C.

#### 4.1.2. Binary Ti-Si – system

##### 4.1.2.1. As-cast state

The binary Ti-Si-alloys studied in this work as model in order to estimate better the influence of additional alloying with Zr, Al etc. demonstrate relatively not bad plasticity in field of solid solutions, which decreases sharply (practically to zero at an arise of excessive silicide phase at crystallization at content of around 2-wt. % Si and increase slightly to 0.4 % at arise of eutectic constituent at silicon content around 4-wt. %).

The data on elongation ( $\delta$ ) and tensile strength (UTS) of binary Ti-Si system tested at room temperature (RT) together with literature data [11] are summarized in Fig. 1. As it is seen an increase of silicon content to 2.0- wt. % decreases plasticity of as-cast BT1-0 alloy from around 6 % practically to zero whereas its strength increases from around 762 MPa to 892 MPa. Further increase of silicon content results in some negligible increase of plasticity and strong increase of strength up to 982 MPa where it reaches its maximum at 4.0-wt. % Si.

Low plasticity of as-cast state in alloys with content of silicon higher 2 % results from a few reasons:

1. In alloys with 2-wt. % Si, the closed extended network of brittle silicides along grain boundaries arises. It is embrittling alloy and results in brittle intergranular fracture. At increase of silicon to 8 %, a eutectic structure with dendritic silicide structure is forming.



Change of fracture mechanism for transcrystalline one is not accompanied by notable increase of plasticity. Deformation of such alloys with no failure of silicides is practically impossible, that is limiting plasticity; besides that cleavage extended facets at separate elements of ductile fracture may be noted.

2. The second reason is oversaturation of as-cast solid solution with silicon that confirms by change of lattice parameter. After annealing at 700-850 °C this parameter recovers to equilibrium ones however it is not accompanied by significant increase of plasticity.

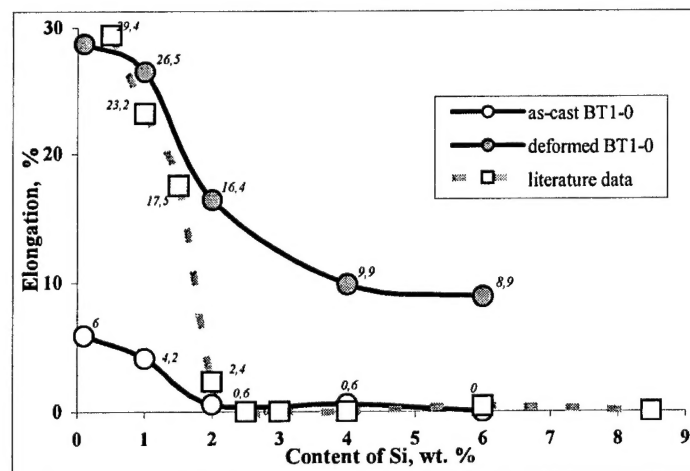


Figure 2. Room temperature plasticity of as-cast and deformed commercial BT1-0 alloy vs. Si content in it. Literature data on as-cast alloys are taken from [11].

#### 4.1.2.2. As-deformed state

Thermomechanical treatment results in notable increase of plasticity that connected with failure of continuous silicide frame for separate silicides. Hot plastic deformation with forging at 1050 °C changes the behavior of all alloys of the Ti-Si-system favorably. As it is seen the elongation of forged alloys decreases with silicon increase not so drastically as in as-cast state namely from 31-32% in original BT1-0 alloy only to 8-9% in Ti-5.7wt. % Si alloy practically monotonously. Structure of such alloys in deformed state reminds structure of DRTi composites like shown in Fig. 3. Fracture mechanism becomes ductile and a margin of plasticity is such that significant additional strengthening with alloying is possible. It is shown that plasticity of alloys with silicon content  $\leq 2\%$  Si overcomes 18 %, and of alloys with silicon content  $\geq 2\%$  Si consists of 8-9 % after deformation and annealing. In that time, strengths of deformed binary alloys containing 2-, 4- and 6-% Si at temperatures 600 and 750 °C are practically coinciding. Therefore, for optimal ratio combination of characteristics of strength, plasticity and heat resistance alloys with 2 % Si are more suitable because the margin of their plasticity is much higher than of alloys with 4- and 6-% Si. It is important: all the deformed Ti-Si-alloys fail with ductile "cup and cone" way evidencing their high ductility potential.

This result is the base of a further search of optimal alloying of Ti-Si-alloys for further alloying of combination of their mechanical properties.

#### 4.1.3. Complex alloyed Ti-Si – system

The above study shows clearly that alloying titanium of technical purity (alloy BT1-0) with silicon may ensure tensile strength around 1050 MPa at around 9 % of elongation (Fig. 2). It

means that a margin to enhance these properties with alloying by other elements like aluminum and zirconium traditionally introduced to improve high temperature properties of titanium.

#### 4.1.3.1. As-cast state

Structure and some mechanical properties of ingots of alloys of Ti-Si-Al-, Ti-Si-Al-Zr-systems with selected ingots of the Ti-Si-Al-Zr-system containing 3.0-wt. % Al and 5-wt. % Zr, and 4.0- and 6.0-wt. % Si were studied. was studied influence of modification (Tasks 6 and 10), additional alloying with V, Nb, Mo (Task 10). Besides that it was studied structure and properties of some multicomponent alloys with heat resistant matrix Ti-6Al-5.5Zr-2.5Sn-1Mo-1Nb alloyed additionally with Si. Some simple Ti-Si-Mo, Ti-Si-Zr, and Ti-Si-Hf alloys were studied too. Content of Al was varied in wide limits (up to 14-wt. %).

Main ideas, which were put in a base of study of structure and properties of this group of alloys, are to investigate possibilities to improve combination of properties of alloys with  $\alpha$ -,  $\alpha+\alpha_2$ -matrixes,  $\beta$ -matrix.

For alloys with alloys with  $\alpha$ - and  $\alpha+\alpha_2$ -matrixes basic alloying elements are Zr and Al. Structure and some mechanical properties of ingots of alloys of Ti-Si-Al and Ti-Si-Al-Zr-systems were studied.

Compositions of the alloys studied are shown in Annex 1.

It is necessary to note that alloying with Al results in some roughening silicide phase, however alloying with Zr, contra, makes them more dispersive. Moreover, at Zr content above 6 %  $(\text{Ti,Zr})_2\text{Si}$  phase arises, and at increase Zr content to 18 % the eutectics forms with this silicide. Varying Al content the change of ratio between these silicides is possible. E.g., in alloy with around 3 % Al at content of Zr 18 % the mixture of silicides  $(\text{Ti,Zr})_5(\text{Si,Al})_3$  and  $(\text{Ti,Zr})_2(\text{Si,Al})$  is observed, and increasing Al content the eutectic built with phase  $(\text{Ti,Zr})_5(\text{Si,Al})_3$  silicide is recovered. According to hot hardness data, in the group of alloys under consideration the alloys built on the  $(\text{Ti,Zr})_5(\text{Si,Al})_3$  silicide base and rather high Al content are differing with the highest heat resistance (Table 3.1.2.1. of Task 10). Alloys built with the  $(\text{Ti,Zr})_2(\text{Si,Al})$  silicide are differing with enhanced strength because strength of as-cast Ti - 2.7-% Al - 5.6-% Si - 18-% Zr-alloy reaches 1400 MPa, however alloys with the  $(\text{Ti,Zr})_2(\text{Si,Al})$  silicide have lower heat resistance in comparison with alloys built with the  $(\text{Ti,Zr})_5(\text{Si,Al})_3$  silicide.

Alloying with V, Mo and Nb is accomplished with decreasing both heat resistance of composites under study and their Young modulus. I.e., introducing  $\beta$ -phase in structure, as well as full transition to  $\beta$ -matrix too, does not allow good combination of heat resistance and stiffness of in situ composites.

Alloys with  $\alpha$ -matrix strengthened with the  $(\text{Ti,Zr})_5(\text{Si,Al})_3$  silicide and additional enough alloying are distinguishing with the highest strength at elevated temperatures. E.g., alloy Ti-6Al-5.5Zr-2.5Sn-1Mo-1Nb-6Si has at 800 °C strength of 336 MPa that overcomes strength of analogous alloy with no Si at the same temperature. Alloys with  $\alpha+\alpha_2$ -matrixes are looking perspective at increased content of Al (up to 12-14 %).

In such a way, significant increase of a few properties of composites under consideration is possible with complex alloying in comparison with the binary system. However, plasticity of 3-4 % at room temperature looks as impossible.

It is necessary to note that alloying with Al is roughening silicide phase a little, however alloying with Zr, on the contrary, makes it more dispersive. Moreover, phase  $(\text{Ti,Zr})_2\text{Si}$  arises at Zr content above 6 %, and at Zr content 18 % eutectics arises with this silicide. It is worthy to be noted that we are succeeded in improving technology of casting and smelting of compositions, which is differing with plasticity up to 0.5 % in as-cast state.

It was taken attempts to improve structure and properties of alloys with modification. The elements B, Y, Bi, La, Sc, Ce, Ga, Re were chosen as modifiers for group of hypoeutectic alloys of the Ti-Si-Al-Zr-system. The certain dispersion of structure must be noted. Besides that, some decrease of Vickers hardness of composites was found in general, and microhardness of  $\alpha$ -matrix with microalloying Ce, La and Y that is probably possible due to purification of  $\alpha$ -solid solution from oxygen. At optimal concentrations, Ce, Bi, Ga, Y and La allow to get double increase of microplasticity of as-cast alloys. Unfortunately, in general, plasticity of as-cast complex alloyed alloys is low and does not overcome 0.5 %.

It was taken attempts to influence on structure and properties of alloys with changing of conditions of their crystallization (Tasks 3, 4). The experiments were done with Ti-3Al-4Si-5Zr-alloy. It was established that the rate of crystallization does influences significantly of a size of dendrites and dispersity of silicide phase. The increase of rate of crystallization from  $10^0$  to  $10^2$  K/s allows increasing strength, plasticity, and Young modulus. Unfortunately, plasticity keeps low.

Investigation of influence of overheating of a smelt on structure and of alloys reveals some influence and the temperature interval of overheating, which allows better combination of properties in as-cast state, was found. However and in this case plasticity remains at rather low level.

Some increase of plasticity might be reached with heat treatment of ingots. In particular, regimes directed on breakdown of as-cast frame with high temperature annealing in  $\beta$ -area as well as annealing in  $\alpha$ -area. All the kinds of such annealings, albeit improve plasticity of composites, however, and in this case it does not overcome, as a rule, 1-1.5 % at room temperature.

Another types of heat treatment was directed on structural preparation of alloys to the further deformation are considered below.

In such a way, although as-cast in situ composites demonstrate good heat resistance, good strength at low temperatures, and their plasticity remains significantly limited (Table 1). Taking into account that  $\beta$ -alloys do not differ with high heat resistance, it was taken as rational to apply thermomechanical treatment to alloys with  $\alpha$ -matrix.

*Table 1. Effect of different processing on ductility at bending (%) of as-cast Ti-3Al-6Si-5Zr composite at room temperature. The best data are shown.*

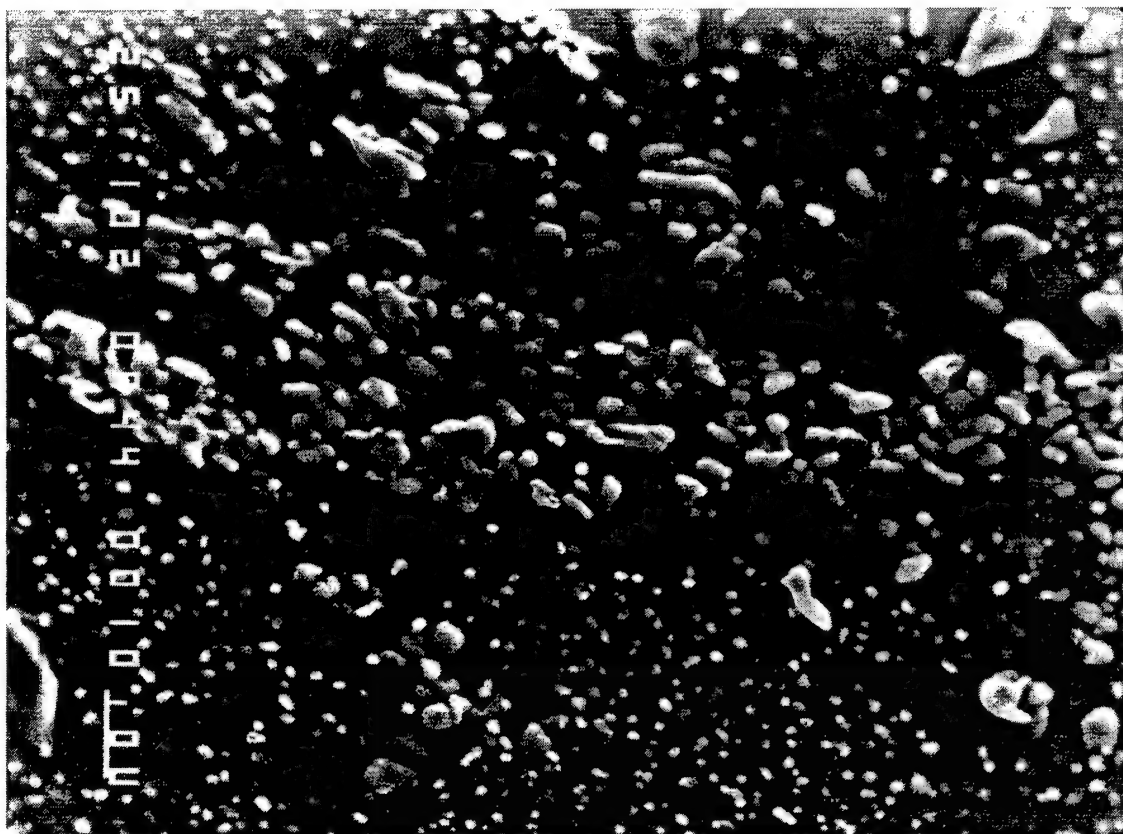
Original casting	Cooling rate	Temperature of melt	Modification	Annealing
0.19%	0.06% at 1.0 K/s 0.20% at 100 K/s	0.1% at 1560 °C 0.01% at 2000 °C	0.49% with 0.08Bi	0.4% at 1300 °C, 4 hours

#### 4.1.3.2. As-deformed state

The investigations were done with two groups of alloys. Initially experiments were done with alloys with 2, 4 and 6 % at 3 % Al and 5-6 % Zr to elaborate regimes of thermomechanical treatment. After deformation regimes were elaborated, compositions were determined to optimize structure and properties of deformed alloys.

At selection of deformation regimes it was found that alloys meet forging, stamping, upsetting at temperatures above 1050 °C.

It was established that, like in binary system, deformation increases significantly in comparison with as-cast state the plasticity at room temperature. After forging for 90 %, plasticity (elongation) of Ti-3Al-5Zr alloyed with 2-, 4-, and 6-wt. % Si consists of 4, 2.8, and 1.8 % respectively (Fig. 4). The decrease of plasticity in comparison with binary system results from both strengthening of solid solution with alloying elements and some increase of fraction of strengthening phase because alloying of silicide with Al, which arranges in silicide lattice on the silicon positions, increases content of phase. Besides that the transition of some content of silicides in  $(\text{Ti,Zr})_2\text{Si}$ -phase was found that, it is possible, is one of the reasons of some increase of strengthening phase after deformation too. As well as in the binary system in four-component alloys it was found that strength of alloys with 2- % Si at increased temperatures practically does not differ on high temperature strength of in situ composites with high silicon content (Fig. 5). Due to this reason the influence of thermo-mechanical treatment on structure and properties of alloys with comparatively small ( $\approx 2$ -wt. %) silicon content was studied in more details.



*Figure 3. SEM appearance of deformed for 90% Ti-2Si-3Al-5Zr alloy.*

Taking into account that at plastic deformation the silicide frame became cracked at the initial stages of deformation the further healing of these cracks with further deformation was studied. As this study shows this reaches at deformation overcoming 80 %. Indeed, in that time as plasticity of alloys after 30 and 60 % deformation does not overcome 1-2 %, after higher deformation the room temperature plasticity overcoming 3 % may be ensured.

At the same time, since, as mentioned above, heat resistance of alloys with 2 % Si in deformed state likes of alloys with increased silicon content, it was clear that in deformed state the optimal structure and properties may be ensured with so-called titanium "steels", Si content of which

does not overcome 2 %. Some possible decrease of heat resistance might be compensated with additional alloying. Due to this reason the influence of thermomechanical processing on structure and properties of alloys with relatively low silicon content was studied in more details.

Since the Ti "steels" allow full dissolving of silicide phase before deformation, additional study of influence of zirconium and aluminum content on possibility of full dissolving of silicides at heating in  $\beta$ -region.

As it followed from the phase equilibrium study, increase of Al and Zr content decreases in some extent the solubility of Si in matrix. Being based on this finding the experiments on quenching of alloys of the Ti-Si-Al-Zr-system where Zr and Al content was varied from 3 to 8 % were done.

It was shown that at an increase of Zr and Al above 5-6 %, Si content must be limited by 1.8-1.9 %. These alloys may have one phase structure in  $\beta$ -region.

Advisability of production of such the structures before the further deformation was shown by the experiments as the next. It was found that preliminary quenched alloys of Ti-5Al-1.9Si-4Zr composition after quenching from 1300 °C allowed plastic deformation with rolling at 750 °C with no cracking. In that time edges and surface of rolled semi-finished blanks rolled at the same regimes reveal cracks.

In general structure and properties of alloys of the Ti-Si-Al-Zr-system of wide spectrum of compositions were studied. Compositions and properties of number of studied alloys are shown in Annex 2.

As it is seen in Annex 2 the alloy Ti-8.4Al-1.4Si-2.4Zr after forging in  $\beta$ -range (1050 °C) as well as after rolling at 1065 °C characterizes by good combination of properties. Namely, yield stress and strength are 817 MPa and 866 MPa at 600 °C, and at 700 °C – around 600 MPa and 630 MPa respectively. Plasticity is relatively high – 1.6-1.8 % and fracture toughness does not overcome 20 MPa. However, plastic deformation being finished in  $\alpha$ -region leads to significant increase of plasticity at room temperature – 6 %, and fracture toughness reaches 50 MPa·m<sup>1/2</sup>. Analogous picture was observed in T23 alloy (Ti-8.66Al-1.2Si-3.8Zr).

Let us note the difference of structure of alloys deformed in  $\alpha$ -region and in  $\beta$ -regions. In alloys fully deformed in  $\beta$ -region in  $\beta$ - $\alpha$  transformation after completion of deformation the thin lamellar structure of  $\alpha$ -phase separated with thin layers of  $\beta$ -phase. Such alloys differ by increased strength, higher high temperature strength, however fracture toughness of such alloys remains on level of as-cast alloys and does not overcome as a rule 20 MPa·m<sup>1/2</sup>. In that time, alloys, plastic deformation of which was finished in region of stable  $\alpha$ -phase, have relatively equiaxial deformation substructure, do not contain signs of martensitic transformation and differ by very good combination of strength, plasticity at room temperature and fracture toughness. Experiments to study an influence of some parameters of heat treatment after deformation on structure and properties of alloys were done.

Slow cooling of alloys with high content of Al from temperature 980 °C and 800 °C decreases a little plasticity (up to 3.6-3.8 % that, as it seen, overcomes the Project's task), quenching from 980 °C in water allows to get rather high plasticity (6.4 %). As the study shows such the difference is due to precipitation of dispersive  $\alpha_2$ -phase at annealings. In that time it does not form at quenching that allows so remarkable plasticity.

Alloy Ti-30Mo-1.6Si demonstrates good plasticity at room temperature (8.8 %) after deformation. Unfortunately other properties like Young modulus, heat resistance are rather low.

Alloy Ti-5.8Al-4Zr-0.5Mo-2.5Sn-0.8Nb-1.7Si has good plasticity at room temperature. Its plasticity is 11.8 % (Annex 2).

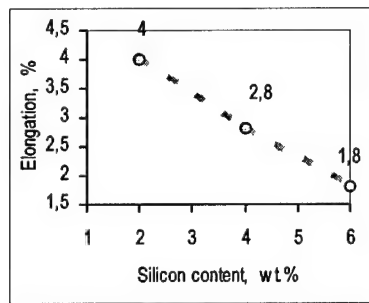


Figure 4. Room temperature plasticity (elongation at uniaxial tension) of forged for 90 % Ti-3Al-5Zr vs. Si content.

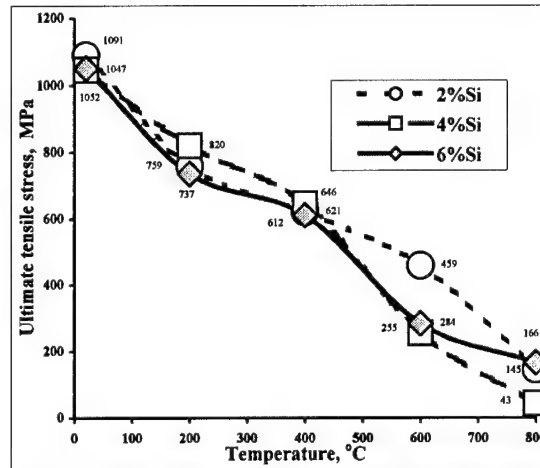


Figure 5. Temperature dependencies of strength (a, b) and elongation (d, c) of the +2Si, +4Si and +6Si alloys in as-cast (a, c) and forged (~90% strain) (b, d) conditions.

Ti-alloys being heated in air at high temperatures are subjected to oxidation. Some saturated with gases layer having higher hardness and lower plasticity is formed on their surface.

The comparative test on influence of oxidation of commercial Ti-7.1Al-2.5Mo-3.6Nb-2.7W-1Zr-0.5Si and developed Ti-8.5Al-1Si-1.3Zr alloys were annealed in air for 1 hour at temperatures 600 and 700 °C. Data on the tensile tests of alloys named at room temperature in initial state and after annealing are shown in Table 2.

Table 2. Data on influence of oxidation on strength and plasticity of conventional (Ti-7.1Al-2.5Mo-3.6Nb-2.7W-1Zr-0.5Si) and developed (Ti-8.5Al-1Si-3.1Zr) alloys.

Alloys	State before oxidation	Properties			Temperature of oxidation, °C	Properties after oxidation		
		$\sigma_b$ , MPa	$\sigma_{0.2}$ , MPa	$\delta$ , %		$\sigma_b$ , MPa	$\sigma_{0.2}$ , MPa	$\delta$ , %
Ti-7.1Al-2.5Mo-3.6Nb-2.7W-1Zr-0.5Si	Rolling	1059	915	2.6	600	895	-	0
					700	766	-	0
Ti-8.5Al-1Si-3.1Zr	Rolling+profile rolling, 950°C + annealing 800°C, 1 hour	1316	1240	7.8	600	1310	1220	5.6
					700	1320	1210	8.1

It is seen that strength and plasticity of alloy, which contains higher silicon, did not change after annealing. In that time, these properties of commercial alloy was changed significantly; strength decreased and plasticity dropped to zero.

It was shown that quenching promotes plastic deformation, i.e. their ability to be deformed and homogenized.



As the most important and encouraging results obtained, the development of which could led to properties desired and which was put into the base for optimization of this group of Ti-Si-alloys during the third year of study, were as follows (Table 3):

*Table 3. Data on influence of type of thermomechanical processing on mechanical properties of Ti-S-X-composites with a sample Ti-8.0Al-2.2Zr-1.4Si.*

Property	forging and annealing at 800°C, 2 hours	deformation finished in $\beta$ -temperature region	deformation finished in $\alpha$ -temperature region
RT strength, UTS, <i>MPa</i>	<b>1302</b>	1182	1234
600°C strength, UTS, <i>MPa</i>	--	<b>923</b>	608
700°C strength, UTS, <i>MPa</i>	<b>632</b>	<b>653</b>	409
RT elongation, $\delta$ , %	1.83	2.1	<b>6.1</b>
RT fracture toughness, $K_{Ic}$ , <i>MPa<math>\cdot\sqrt{m}</math></i>	--	19.2	<b>51.1</b>
RT fracture mechanism	<b>void coalescence</b>		

## 4.2. Ti – B – SYSTEM

### 4.2.1. Phase equilibrium diagrams

The ternary alloys Ti-Al-B, Ti-Si-B, Ti-Ge-B, Ti-Sn-B, Ti-V-B, and Ti-Nb-B, as well as quaternary Ti-Al-Si-B, Ti-Al-Ge-B, Ti-Al-Sn-B, Ti-Al-Zr-B, Ti-Al-V-B, and Ti-Al-Nb-B were studied in order to construct phase diagrams in the Ti corners at melting temperatures and to estimate mechanical characteristics.

Data obtained on the extensions of two-phase Ti+TiB fields at subsolidus temperatures are summarized in Table 4. For the as-cast alloys the two-phase regions are more restricted.

*Table 4. Extensions of two-phase Ti+TiB fields in the Ti-B-X ternary systems at solidus temperatures*

System	Content of alloying element (at.%) in phases of tie-line restricting the (Ti) + (TiB) two-phase field		Solidus temperature (°C)
	Metal matrix	Monoboride	
Ti-Al-B	37	undetected	1540
Ti-Si-B	3.0	undetected	1325
Ti-Ge-B	7	undetected	1322
Ti-Sn-B	13	~0.1	1575
Ti-V-B	40	25	1460
Ti-Nb-B	~57	~30	~1800

Basing on the results of this investigation on phase equilibrium, the following are the key observations:

- i) The alloying additions under studying do not affect specific titanium-boride two-phase Ti+TiB eutectic structure in wide content ranges.
- ii) The alloying initiates a little change in the eutectic compositions; *p*-elements (Al, Si, Ge, and Sn) reduce the boron content in the eutectic by ~1-2 at. % and *d*-metals (Zr, V, and Nb) rise by ~1-2 at. % B, i.e. slightly increased boride content in the eutectic is characteristic of the alloys  $\beta(\text{Ti,V}) + (\text{TiB})$  or  $\beta(\text{Ti,Nb}) + (\text{TiB})$ .

Partition of alloying elements between titanium matrix and boride phases is radically different for *p*-elements and *d*-elements:

- i) *p*-elements (Al, Si, Ge, and Sn) dissolve fully in matrix;
- ii) *d*-elements (Zr, V, and Nb) partition comparably between titanium and boride phases.

The effect of *p*-elements and *d*-elements on Vickers hardness (therefore strength) was analyzed in the temperature range from room temperature (RT) to 800 °C. Toward this end, a number of alloys were melted at the constant boron content of 7.5-at. % for the ternary and quaternary systems under studying. Another special approach was elaborated that is founded on

comparisons of alloys' property, basing on a hierarchical principle. The comparison of hot hardness curves of the ternary alloy  $\text{Ti}_{84}\text{Al}_{8.5}\text{B}_{7.5}$  with all the two appropriate binaries ( $\text{Ti}_{92.5}\text{B}_{7.5}$  and  $\text{Ti}_{90}\text{Al}_{10}$ ) makes clear the contributions of the both factors, the Al solid solution strengthening and boride reinforcement. In the same manner one can reveal contributions of each addition to quaternary alloy properties, comparing with appropriate ternaries.

Each of alloying additions were found to contribute to hot hardness of ternary, quaternary and multicomponent alloys, although the total hardening effect is mainly somewhat less than the sum of all separate contributions. *p*-Elements and Zr have effect at all the temperatures under studying. The maximal strengthening was determined at the alloying with Si and Ge. In contrast to *p*-elements, the alloying with  $\beta$ -stabilizing elements V and Nb increases hardness up to  $\sim 400^\circ\text{C}$  (ternary alloys) or to  $\sim 600^\circ\text{C}$  (quaternary and multicomponent alloys). But at higher temperatures this property degraded, for the exception of the ternary alloy containing much V (45 at. % V), of which hardness at  $700^\circ\text{C}$  is quite high, equal to 1 GPa. Taking into account that the volume content of reinforcing boride phase, its dispersivity and properties practically do not change at the alloying, the strengthening of the ternary and quaternary eutectic alloys with the alloying elements under studying should be attributed to the solid-solution strengthening of their matrix practically in full.

Comparing the consecutive series of alloys containing the same metal matrix, one can see the contributions of the boride reinforcement in hypoeutectic and eutectic alloys, i.e. on comparing with the unalloyed boron-free alloy, e.g.  $\text{Ti}_{90}\text{Al}_{10}$ . The boride reinforcement contributes well to hot hardness (0.5-1 GPa) up to the temperature of sharp softening and depends on its volume content. The boride reinforcement offers a great potential in strengthening of conventional high-temperature titanium alloys from RT up to the upper-range temperature of their application (the augmentation in hot hardness is by  $\sim 0.5$  GPa up to  $600^\circ\text{C}$ ).

#### **4.2.2. Binary Ti – B – system**

##### **4.2.2.1. As-cast state**

The Ti-TiB eutectic is characterized by the space skeleton of reinforcing phase analogous to a regular one. The volume fraction of boride reinforcing phase is almost unaffected by alloying and is within a range from 9.5 to 10 vol. %.

Strength of as-cast Ti-B-alloys growth monotonically with increasing boron content showing maximal strength between 1- and 2-wt. %.

The as-cast TiB-alloys demonstrate room temperature plasticity 2.5 % (elongation) at 1.5-wt. % B.

##### **4.2.2.2. As-deformed state**

A few alloys were smelted based on commercial titanium (BT1-0) alloy (Annex 3), which were used for deformation. The best results shown in Table 5 were obtained with Ti-1.6-wt. % B-alloy.

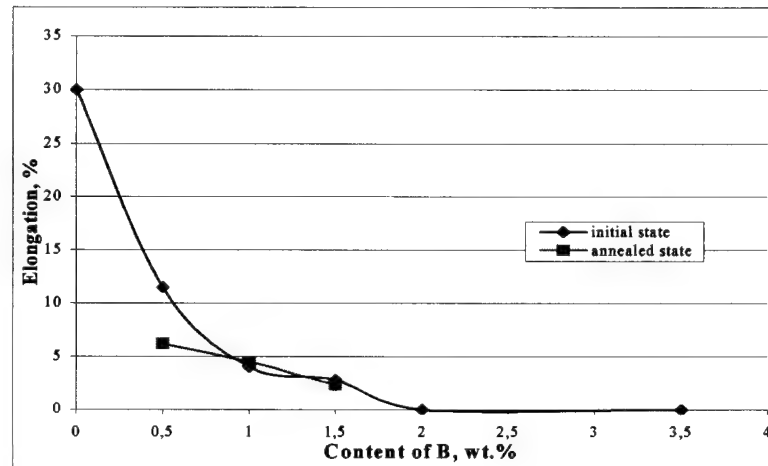


Figure 6. Mechanical properties of cast and annealed Ti-B (wt. %) alloys.

Table 5. Mechanical properties of Ti-1.6B alloy.

Properties of alloy	<i>as-cast</i>	<i>deformed</i>
Yield strength, $\sigma_{0.2}$ , MPa	900	944
Strength, UTS, MPa	904	977
Elongation, $\delta$ , %	0.4	<b>6.4</b>
Fracture mechanism	cleavage and void coalescence	<b>void coalescence</b>

The strong increase of RT plasticity with deformation must be noted.

#### 4.2.3. Complex alloyed Ti – B – system

It was found (The 2<sup>nd</sup> year report, Task 9a, p.54) that alloying with Al, Si, Ge, Sn results in significant strengthening of ternary and quaternary alloys.

Stiffness is one of the most important properties of Ti-alloys under study. Table 3 shows elasticity modulus for different ternary and quaternary compositions. It is seen that Ti-B- alloys alloyed with Si and Ge have the highest modulus up to 167 GPa.

##### 4.2.3.1. As-cast state

For all alloys the thermo-activation analysis of the temperature dependence was carried out in order to determine the mechanism of high temperature softening and incipient temperature of the latter. On replotting dependences HV vs. temperature in the  $\ln(HV)$  vs.  $(-1/T)$  coordinate, they take linear shape in a temperature range of single apparent activation energy. Determination of

activation energy for a deformation (within the accuracy of available data) allows making conclusion on the deformation mechanism.

Three linear intervals of  $\ln(HV)$  vs.  $(-1/T)$  dependences clearly seen were revealed. The activation energy of deformation (flow) during Vickers pyramid submerging in sample was found to be in the range 2 to 8 kJ/mole for the low temperature interval from RT to 300-400°C (1). At intermediate temperatures 300 to ~500°C (2) the energy is about 20 kJ/mole, and at higher temperatures (3) the activation energies are ~100 to 210 kJ/mole. The temperature point between (2) and (3) regions, corresponding to transition from nondiffusional mechanism to diffusional one that control deformation (flow), is of importance since it practically coincides with the upper-range temperature of application. It is the incipient temperature of sharp softening of alloys, which might be considered as transition temperature.

The boride reinforcement does not affect transition temperature. The 2.6-at. % Sn content in an alloy (i.e. 3 at. % Sn in the matrix) increases the transition temperature by ~50°C. The action of Si and Ge additions are almost the same, and the 8.5-at. % Al alloying in an alloy (i.e. 10-at. % Al in the matrix) increases the transition temperature by ~100°C. So, the latter is fully dependent on the alloy matrix and can be enhanced from ~500°C (for the binary Ti-B alloy) to ~650°C (as for the alloys IMI 834 and Ti-1100) by rational alloying.

The best data obtained with as-cast complex alloyed Ti-B-alloys smelted on industrial BT1-0 base are shown in Table 6.

#### 4.2.3.2. As-deformed state

Table 6 shows the best properties obtained with deformed complex alloyed alloys of the Ti-B-system.

*Table 6. Mechanical properties of complex alloyed alloys of the Ti-B-system.*

Composition of alloys	Ti-3Al-1.2B, arc melt.		Ti-4.5Al-1.9B, electron beam melt.		Ti-3Al-1.3B-5Zr, arc melt.	
	<i>as-cast</i>	<i>deformed</i>	<i>as-cast</i>	<i>deformed</i>	<i>as-cast</i>	<i>deformed</i>
Properties of alloys						
Yield strength, $\sigma_{0.2}$ , MPa	1000	972	-	1140	-	1055
Strength, UTS, MPa	1020	1033	-	1184	993	1082
Elongation, $\delta$ , %	1.4	7.2	-	6.24	-	1.6
Young modulus, E, GPa	144	138	138	152	147	136
Fracture mechanism	cleavage and void coalescence	cleavage and void coalescence	void coalescence	cleavage and void coalescence	cleavage and void coalescence	void coalescence

### 4.3. Ti – Si – B – system

#### 4.3.1. Phase equilibrium diagrams

The Ti-Si-B alloys were studied at Si content up to ~11 at. %. The partial Ti-Si-B phase diagram is presented in Fig. 7. Silicon is not practically dissolved in the TiB boride, concentrating fully in the metal matrix and in a ternary silicidoboride when it forms. This ternary silicidoboride of referred to  $Ti_6Si_2B$  composition [12,13] was found to be present as high dispersed phase (around 200 nm) in the three-phase eutectic (Ti) +  $Ti_6Si_2B$  + TiB that solidifies at 1320°C. The ternary eutectic alloy hardness vs. temperature shows that it offers a great potential in a comparison with the binary (Ti) + TiB and (Ti) +  $Ti_5Si_3$  eutectics (Fig. 8).

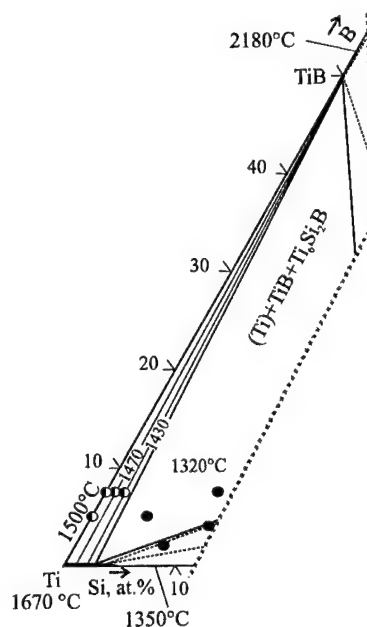


Figure 7. The Ti-Si-B solidus projection in the Ti-rich corner.

#### 4.3.2. Complex alloyed Ti – Si – B – system

It was seen above that titanium alloyed with boron and silicon has high strength and Young modulus, and has high ductile potential because fails with ductile fracture mode.

The Ti-6.6Al-3.5Zr-1.3Si-1.1B alloy was smelted and studied.

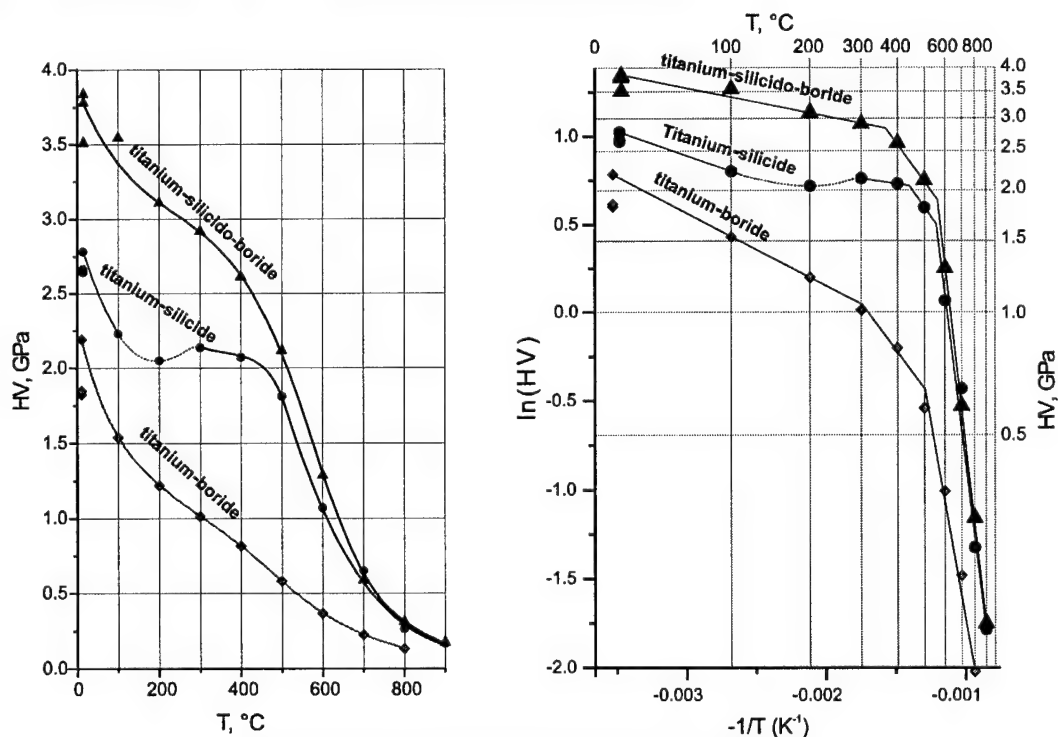


Figure 8. Hot Vickers hardness of eutectic alloys.



#### 4.3.2.1. As-cast state

In as-cast state, as-dendritic structure is practically invisible. Lamellar  $\alpha'$ -structure of matrix is recognized well (Fig. 9). Close to uniformly distributed borides have rod-like morphology and fogged like brushwood. Thickness of rods is between 0.1-1.5  $\mu\text{m}$ . Their length is up to 0.2 mm. Fine (0.1-0.3  $\mu\text{m}$ )  $\text{Ti}_6\text{Si}_2\text{B}$  are uniformly distributed along matrix. Fracture feature is intensive cleavage microcracking of RT and 600  $^{\circ}\text{C}$  samples. Delamination of borides from matrix is not observed that evidences the high adhesion between borides and matrix.



Figure 9. TEM appearance of silicoborides  $\text{Ti}_6\text{Si}_2\text{B}$  in Ti-11Si-4B alloy.

#### 4.3.2.2. As-deformed state

In as-forged state, structure of matrix is close to polygonal. Crashed borides form chains of particles of rod and strip morphology. It is strange but it is seen that boride strips are often splitted for three ones. Preliminary qualitative x-ray microanalysis shows that borides are compounds containing, except boron and titanium, all the additives added specially like Al, Si, Zr, and present in the basic BT1-0 alloy like Fe, O and possibly C. Matrix, to our surprise, is pure in comparison with original BT1-0 alloy. Matrix, unexpectedly, consists of Ti, Al, Si, and Zr only. Thickness of silicides likes to as-cast one. Fracture of this forged alloy at room temperature and 600  $^{\circ}\text{C}$  is ductile one and uniform. It is clear that some unhealed cleavage cracks of matrix as well as broken particles, silicides and borides, may be found yet in both samples.

As Table 7 shows deformation is strongly improve mechanical properties of the Ti-Si-B-system too.

The presence of borides and silicoborides is the main reason of stiffness increase of the Ti-Si-B-X composites shown in Fig. 10 where typical data on Young's modulus of different boron containing alloys. It is clearly seen that new strengthening  $\text{Ti}_6\text{Si}_2\text{B}$  phase is very promising for stiffness enhancement.

Table 7. Mechanical properties of Ti-6.6Al-3.5Zr-1.3Si-1.1B alloy.

Properties	<i>as-cast</i> <i>tested at RT</i>	<i>deformed</i>	
		<i>tested at RT</i>	<i>tested at 600°C</i>
Yield strength, $\sigma_{0.2}$ , MPa	-	1470	550
Strength, UTS, MPa	843	<b>1530</b>	<b>590</b>
Elongation, $\delta$ , %	-	1.4	7.8
Young modulus, E, GPa	141	<b>159</b>	-
Fracture mechanism	cleavage and void coalescence	<b>void coalescence</b>	void coalescence

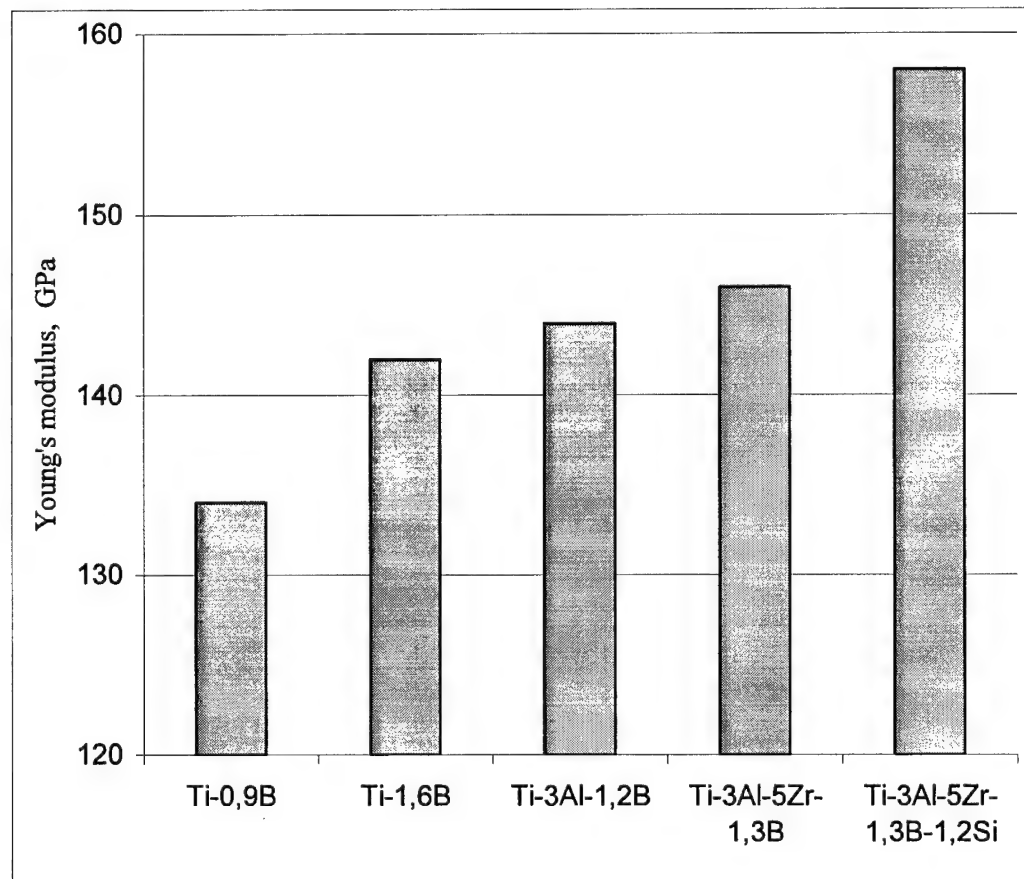


Figure 10. Typical data on Young's modulus of different boron containing deformed alloys.

## 5. CONCLUSIONS

1. Phase and structural compositions of the Ti-Si-X and Ti-B-X systems, where X are Al, Zr, Nb, V, Mo, W, Sn etc., which are the base of development of new class of in-situ composites based on titanium, are studied.
2. In dependence of content of silicon in situ composites may be classified in accordance with diagrams of phase equilibrium on two groups namely "titanium cast iron" and "titanium steels". In the first group (Si content is 2-8-wt. %) the strengthening phase is formed during eutectic crystallization. In the second group (Si content is 0.5-2-wt. %) – during phase transformations in solid state.
3. Strengthening phase in eutectic alloys in dependence on additional alloying (Zr and Al have special influence) is of two types namely  $(\text{Ti,Zr})_5(\text{Al,Si})_3$ , and  $(\text{Ti,Zr})_2(\text{Al,Si})$ .
4. Matrix of alloys in dependence on alloying may change from  $\alpha$ ,  $\alpha+\alpha_2$  to  $\alpha+\beta$ ,  $\beta$ , and intermetallic matrix ( $\text{Ti}_3\text{Al}$ ,  $\text{Ti}_2\text{NbAl}$  etc.).
5. The highest heat resistance in alloys studied is reached in Ti-Si-X-alloys. From the point of view the achievement of the highest heat resistance in as-cast state at keeping of desired plasticity, the most attractive is "titanium cast iron" with  $\alpha$ - and  $\alpha+\alpha_2$  matrixes. Plasticity of such the alloys is significantly limited. Among as-cast materials composites strengthened with  $(\text{Ti,Zr})_2\text{Si}$  phase have some perspective; RT plasticity ~% at bending is reached.
6. Composites of the Ti-B-X and Ti-B-Si-X systems are attractive to obtain materials with high specific stiffness, which is reached due to introduction of TiB and  $\text{Ti}_6\text{Si}_2\text{B}$  phases during eutectic crystallization. Plasticity of as-cast alloys of these systems is higher in some extent in comparison with the Ti-Si-X system, however in general it does not overcome 2-2.5 % in as-cast state.
7. Thermomechanical treatment directed on a change of structure, formed at crystallization, - crashing of frame of strengthening phases, removing inner stresses, healing of pores and cracks of crystallization origin – significantly improve combination of all the mechanical properties, plasticity especially, and fracture toughness. Structure becomes similar to DRTi-composites – matrix strengthened with short filaments of borides and silicides.
8. Among alloys of Ti-Si-X alloys as the most interesting are data obtained with Ti-steels where approaches of thermomechanical treatment developed for Fe-C-steels (carbon steels) may be applied due to proximity of phase diagrams of Ti-Si and Fe-C. On the base of accurate definition of content of alloying elements the compositions and processing when plasticity is in the interval (5-11 %), strength at tension (1100-1400 MPa), strength at bending and compression (1300-1800), strength at 700 °C (653 MPa) were found at Young's modulus 130-136 MPa. It is proved that in contrast to heat resistant alloys with low Si content – 0.5 %, alloys with 0.5-2 % Si are not embrittling after annealing in air at 700 °C.
9. In alloys of Ti-B-X and Ti-B-Si-X the improved combination of specific strength and stiffness was obtained. It is proved that formation of TiB phase and  $\text{Ti}_6\text{Si}_2\text{B}$  especially, allows, in combination with additional alloying with Al, significantly improve Young modulus ~160 GPa at keeping RT plasticity.
10. In such a way, the main tasks planned by the Project – achievement of plasticity exceeding 3 %, improving heat resistance – were achieved. Scientific approaches to formation of new class of materials – titanium steels, which differ by enhanced combination of strength, heat resistance and plasticity.

## ACKNOWLEDGEMENTS

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**Annex 1. List of alloys of the Ti-Si-X-system smelted in big ingots**

# alloy	Chemical composition	melting	size
64	Ti-4,5Si	arc melting	Ø60; h=180
0-44	Ti-0,14 Si	arc	Ø60; h=180
1-45	Ti-1,18 Si	arc	Ø60; h=180
2-46	Ti-2,1 Si	arc	Ø60; h=180
4-47	Ti-3,57 Si	arc	Ø60; h=180
6-48	Ti-5,68 Si	arc	Ø60; h=180
6-49	Ti-2,9 Al-5,9 Si	arc	Ø60; h=180
4-50	Ti-2,6 Al-4,3 Si	arc	Ø60; h=180
4-51	Ti-3,0 Al-2,0 Si	arc	Ø60; h=180
4-52	Ti-3,0 Al-3,6 Si-3,7 Zr	arc	Ø60; h=180
6-53	Ti-2,9 Al-5,8 Si-6,8 Zr	arc	Ø60; h=180
4-54	Ti-2,8Al-3,6 Si-0,3 Zr-8,6 Nb	arc	Ø60; h=180
60-2-2	Ti-0,5Al-2,2 Si-7,2 Zr	arc	Ø60; h=180
60-2-01	Ti-3,0 Al-1,8 Si-4,7 Zr	arc	Ø60; h=180
60-2-02	Ti-2,9 Al-2,04 Si-5,2 Zr	arc	Ø60; h=180
60-2-03	Ti-3,6 Al-2,28 Si-6 Zr	arc	Ø60; h=180
60-2-04	Ti-3,1 Al-2,0 Si-4,8 Zr	arc	Ø60; h=180
60-4-08	Ti-3,0 Al-4,2 Si-5,8 Zr	arc	Ø60; h=180
60-4-09	Ti-3,3 Al-4,2 Si-5,2 Zr	arc	Ø60; h=180
60-4-10	Ti-3,5 Al-4,0 Si-5,5 Zr	arc	Ø60; h=180
60-4-11	Ti-3,0 Al-3,7 Si-5,2 Zr	arc	Ø60; h=180
60-4-12	Ti-3,0 Al-3,7 Si-5,2 Zr	arc	Ø60; h=180
60-4-13	Ti-3,0 Al-3,4 Si-5,1 Zr	arc	Ø60; h=180
60-4-16	Ti-3,4 Al-4,2 Si-5,2 Zr	arc	Ø60; h=180
60-4-17	Ti-3,1 Al-3,8 Si-4,7 Zr	arc	Ø60; h=180
60-4-18	Ti-2,8 Al-3,8 Si-4,6 Zr	arc	Ø60; h=180
60-4-19	Ti-3,0 Al-3,5 Si-4,8 Zr	arc	Ø60; h=180
60-4-20	Ti-2,9 Al-3,6 Si-4,5 Zr	arc	Ø60; h=180
60-4-21	Ti-2,9 Al-3,6 Si-4,5 Zr	arc	Ø60; h=180
60-4-22	Ti-3,0 Al-4,1 Si-5,0 Zr	arc	30x120x120
60-4-23	Ti-2,9 Al-4,2 Si-5,0 Zr	arc	30x120x120
60-4-24	Ti-3,2 Al-4,3 Si-4,9 Zr	arc	30x120x120
60-6-27	Ti-2,8 Al-5,8 Si-5,5 Zr	arc	Ø60; h=180
60-6-28	Ti-3,3 Al-6,0 Si-4,9 Zr	arc	Ø60; h=180
60-6-29	Ti-3,4 Al-5,9 Si-5,1 Zr	arc	Ø60; h=180
60-6-30	Ti-3,4 Al-6,2 Si-4,8 Zr	arc	Ø60; h=180
60-4-32	Ti-3,2 Al-3,7 Si-0,5 Zr	arc	Ø60; h=180
60-6-39	Ti-3,0 Al-5,8 Si-4,7 Zr	arc	Ø60; h=180
60-4-40	Ti-3,0 Al-3,9 Si-0,5 Zr	arc	Ø60; h=180
LM-863	Ti -6 Al - 1,6 Si -5 Zr	EB (Electron Beam)	Ø75; h=400
LM-864	Ti-6 Al-1,6 Si-5,5 Zr-2,5 Sn-1 Mo-1,0Nb	EB	Ø75; h=400
LM-866	Ti-7,1Al - 5,6Zr -1,7Si- 4,5V	EB	Ø75; h=400
LM-898	Ti -9 Al -1,6 Si -2,2 Zr	EB	Ø75; h=400
LM-869	Ti-15Al-1,3Si-7,7V	EB	Ø75; h=400
LM-890	Ti - 30Mo-1,6 Si	EB	Ø75; h=400
LM-905	Ti-8,42Al-1,4Si-2,4Zr	EB	Ø75; h=400
T-23	Ti-8,66Al-1,2Si-3,8Zr	EB	Ø75; h=400
LM-907	Ti-11,8Al-1,9Si-2,2Zr	EB	Ø75; h=400
T-24	Ti-11,2Al-1,2Si-2,6Zr	EB	Ø75; h=400
LM-928	Ti-5,5Al-3,2Si-5,5Zr	EB	Ø75; h=400
LM-680	Ti-6Al-4,9Si-5,4Zr	EB	Ø75; h=400
T-27	Ti-7,8Al-1,5Si-4,8Zr-2Sn-1Mo-1Nb	EB	Ø75; h=400
LM-922	Ti-7,4Al-0,2Si-4Zr-3Sn-0,4Mo-1Nb	EB	Ø75; h=400

**Annex 2.**

**Table 1. Mechanical properties of alloys LM-905 (Ti-8.0Al-1.4Si-2.2Zr) and T-23 (Ti-8.5Al-1.0Si-3.1Zr) after different thermomechanical treatment**

Ingots	$\sigma_{0.2}$ , MPa		$\sigma_b$ , MPa		$\delta$ , %			E, GPa			$K_{IC}$ , MPa·√m		
	Temperature, °C												
	20	600	700	20	600	700	20	600	700	20	20		
LM-905 (Forging 1050 °C + Annealing 800 °C 2h)	1245	817	603	1302	866	632	1.8	6.6	11.4	133	22		
LM-905 (Rolling 1065 °C + Profile rolling 1065°C+Annealing 800 °C 2h)	1100	808	609	1188	923	653	1.6	8.4	18.8	130	19		
LM-905 (Rolling 1065 °C + Profile rolling 970 °C+Annealing 800 °C 2h)	1185	542	328	1234	608	409	6.1	18	28.6	125	50		
T-23 (Rolling 1065 °C + Profile rolling 1065°C+Annealing 800 °C 2h)	1085	636	575	1177	682	597	1.6	12	14.8	128	24		
T-23 (Rolling 1085 °C + Profile rolling 950 °C+Annealing 800 °C 2h)	1130	364	274	1212	424	371	6.6	19	25	125	46		



Table 2. Mechanical properties of forged selected Ti-Si-X-alloys at tension.

Mark	Chemical composition	$\sigma_{0.2}$ , MPa			UTS, MPa			$\delta$ , %		
		Temperature, °C								
		20	600	700	20	600	700	20	600	700
LM-905	Ti - 9Al - 2.2Zr - 1.6Si)	1245	817	603	1302	866	632	1.83	6.6	11.4
LM-864	Ti - 5.8Al - 5.4Zr - 0.5Mo - 2.5Sn - 0.8 - Nb - 1.7Si	1121	456	351	1212	526	448	11.4	7.4	17.8
LM-866	Ti-7.1Al - 5.6Zr - 4.5V-1.7Si	1053	358	284	1145	525	336	5.2	11.8	17.8
LM-863	Ti - 6.3Al - 5Zr - 1.8Si	1120	300	238	1220	338	329	5.4	16	19.4
LM-890	Ti-22Mo-1.6Si	1065	292	175	1103	313	234	8.8	7.2	32.6

Table 3. Mechanical properties of selected Ti-Si-X- alloys at bending

Mark	Composition, wt. %	As-cast				Forged at 1050°C and annealed at 800 °C, 2 hours			
		$\sigma_b$ , MPa	$\sigma_{0.2}$ , MPa	$\delta$ , %	E, GPa	$\sigma_b$ , MPa	$\sigma_{0.2}$ , MPa	$\delta$ , %	E, GPa
LM-863	Ti - 6.3Al - 5Zr - 1.8Si	606	-	-	128	1986	1735	1.06	135
LM-864	Ti - 5.8Al - 5.4Zr - 0.5Mo - 2.5Sn - 0.8 - Nb - 1.7Si	726	-	-	123	2233	1640	2.35	131
LM-866	Ti-7.1Al - 5.6Zr - 4.5V - 1.7Si	766	-	-	117	2200	1710	2.64	128
LM-869	Ti-15Al-7.7V-1.3Si	637	-	0.1	125	1164	1104	0.27	134
LM-905	Ti - 9Al - 2.2Zr - 1.6Si	737	-	0.04	125	2050	1980	0.48	140
LM-907	Ti - 14Al - 2.2Zr - 1.6Si	484	-	0.01	143	-	-	-	-
LM-890	Ti-30Mo-1.6Si	865	-	-	100	1890	1450	5.13	104
LM-908	Ti-4Al-4Zr-1.3Si-1.1B	843	-	-	141	1943	1870	0.34	158

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LM-903	Ti-5.5Al - 1.9B	1691	1530	0.62	138	2146	1700	3.16	152
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**Annex 3. List of alloys of the Ti-B-system smelted in big ingots**

# alloy	Chemical composition	melting	size
	Ti-0,9B	arc	Ø60; h=180
	Ti-1,6B	arc	Ø60; h=180
	Ti-3Al-1,2B	arc	Ø60; h=180
	Ti-4.5Al-1.9B	electron beam	Ø75; h=400
	Ti-3Al-1,1B-5,7Zr	arc	Ø60; h=180
	Ti-3Al-1,3B-5,0Zr	arc	Ø60; h=180
	Ti-3,5Al-5,7Zr-1,2Si-1,3B	arc	Ø60; h=180
	Ti-6,6Al-3,5Zr-1,3Si-1,1B	electron beam	Ø75; h=400